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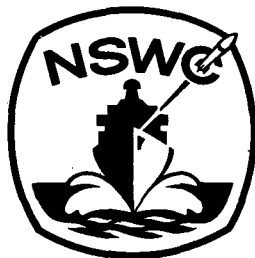
HEXANITROSTILBENE RECRYSTALLIZED FROM NITRIC ACID

BY E. EUGENE KILMER

RESEARCH AND TECHNOLOGY DEPARTMENT

19 SEPTEMBER 1979

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NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

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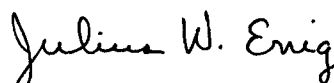
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SUMMARY

Hexanitrostilbene (HNS) was recrystallized by Taylor and Oesterling using dual organic solvents in the early 1960's. Since then, for reasons of economy, nitric acid has been found to be a good solvent for HNS and has been used by industry to replace the more expensive organic solvent method. However, detonation cords fabricated with the nitric acid recrystallized explosive are not as heat resistant as cords prepared with HNS recrystallized with organic solvents. Although, the HNS assays relatively free of nitric acid, it still does not perform as well in detonating cords as the material made from the organic solvent process.

The author wishes to acknowledge Mr. Daniel Polansky for the X-Ray/N-Ray, Ms. Eleonore Kayser for the chemical analyses and nitric acid assays, Dr. Marriner Norr for the scanning electron microscope work, Dr. Joseph Dacons for the HNS recrystallization effort, and Mr. Charles Goode for the detonation velocity study. The identification of commercial materials implies no criticism or endorsement by the Naval Surface Weapons Center.



JULIUS W. ENIG
By direction

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INTRODUCTION

The purpose of this work was to characterize the performance of the explosive Hexanitrostilbene (HNS) recrystallized from nitric acid as a solvent. This method of recrystallization is different from the method described in the Navy procurement specification WS5003F. The original recrystallization process documented by Shipp^{1,2} and Taylor and Oesterling³, described the recrystallization of HNS from dual organic solvents such as acetonitrile-toluene. HNS produced by the dual organic solvent method has been used in many Navy and NASA applications.

In the work reported here, various methods for recrystallization of HNS-I to HNS-II, were evaluated. Explosive material from each one of these methods was made and sent to three different manufacturers for fabrication into detonating cords according to each vendors proprietary process. The explosive was analyzed chemically both before it was sent to the vendor and on receipt of the cords at the Naval Surface Weapons Center (NAVSWC). The explosive cords were characterized while being exposed to conditions of temperature cycling and elevated temperature storage. HNS recrystallized from organic solvents was used as a control standard for detonation velocity performance tests. The results of these tests indicated that the nitric acid recrystallized HNS-II was unacceptable for use in mild detonating cords. The HNS-II recrystallized by the dual organic solvents method was shown to have better thermal stability than the acid recrystallized explosive.

RECRYSTALLIZATION OF HNS

When HNS was first prepared by Shipp, there was considerable concern over the difficulties encountered in the purification of the crude product by recrystallization. This was due to its extremely low solubility in most solvents. Shipp found that the compound could be recrystallized from high boiling organic solvents such as nitrobenzene; however, the crystals consisted of long fine needles which made them extremely difficult to handle. It was then found that by thoroughly washing the crude HNS in such solvents as methanol and acetone, a fine particle size product

containing about 95% HNS could be obtained. Although this material was suitable for some applications, it was very difficult to handle. Moreover, a great deal of the HNS's thermal stability was lost because of the presence of less stable impurities. In an effort to overcome these difficulties, Taylor and Oesterling in 1965 developed a procedure whereby HNS could be recrystallized into a form which had a much higher bulk density and larger particle size than the original product. Therefore, it was much easier to load into hardware because of improved flow properties.

The Taylor--Oesterling recrystallization procedure makes use of an extraction type apparatus with mixed organic solvents (acetonitrile-toluene). HNS is slightly soluble in acetonitrile and essentially insoluble in toluene. When the mixed solvents in the boiling chamber of the apparatus are heated, the more volatile acetonitrile refluxes and returns to the boiling chamber through an extraction compartment containing HNS. As the process continues, the HNS is gradually transferred to the boiling chamber where it crystallizes from the hot mixed solvents. Eventually all of the crude HNS is transferred and recrystallized. On recovery, this product is found to have a much greater bulk density, a considerably higher melting point, and contains considerably less impurities than the crude material.

Soon after the above discovery was made, Syrop⁴ patented a procedure which was very similar where he used acetonitrile-xylene as the mixed organic solvents. The primary claim is that these solvents do not form an azeotropic mixture and are therefore more efficient. This claim was not supported by any findings at NSWC.

The only known solvent which can be used to recrystallize HNS in a conventional manner and produce a product of high bulk density quickly and economically is fuming nitric acid. Unfortunately, much apprehension has developed regarding the use of this solvent. There is considerable feeling that the acid cannot be adequately removed from the crystals. Our studies indicate that this feeling is not justified. We have found that samples of HNS crystallized from nitric acid, properly washed and dried, often show acidities lower than those of samples of HNS which have never been in contact with mineral acids.

All glass equipment and fittings have been used so that the acid does not come in contact with rubber or other materials. A typical example of an acid recrystallization procedure is given below:

A 53_g sample of HNS-I was heated with stirring in 1600 ml of 90% nitric acid until dissolved. The solution was then filtered with suction through a preheated sintered glass funnel into a glass filter flask (all fittings were either glass or teflon). The filtrate was moderately stirred using

a magnetic stirrer and a Teflon coated stirring bar. As the filtrate cooled, crystallization started. Finally, as stirring continued, the receiving flask was cooled in an ice bath for about one half hour. The product was then recovered by filtration. It was washed on the funnel, first with concentrated (70%) nitric acid, then with water and finally with methanol. One half of the product was dried in a vacuum oven at 120°C overnight and the second half was dried for the same length of the time in a warm oven (ca 80°C) under atmospheric pressure.

The above procedure was repeated for a one pound batch. Before drying, the batch was divided, and identified as ID 2302 and ID 2304. Photomicrographs of this material show no change in the appearance of the crystal after the separate drying procedures (see Figure 1). The fraction which was more vigorously surge gave 0.07 cc of gas per gram, and during the two hour period, gas evolution was at the rate of 0.08 cc per gram per hour (see Table 1). The specification requirement is 0.6 cc/g maximum for the 20 minute surge and 0.6 cc/g/hr maximum for the two hour period. The fraction dried in the warm oven at atmospheric pressure failed to meet the requirements for the 20 minute surge, and thereby failed to pass the test. During the following two hour period, gas was evolved at the rate of 0.18 cc/g/hr which is well within the requirements. When this half of the product was dried overnight under vacuum as described above, it passed the test. It thus appears that vigorous drying is essential for HNS-II prepared in this manner. Various other solvents and solvent ratios were tried and tested for vacuum thermal stability. The results of this investigation are shown in Table 1.

Chemical purity was established by High Performance Liquid Chromatography (HPLC) as shown in Table 2. The chemical assays were for hexanitrostilbene (HNS), hexanitrobibenzyl (HNBiB), trinitrobenzene (TNB), trinitrobenzyl alcohol (PiCH₂OH), trinitrobenzaldehyde (PiCHO), and trinitrotoluene (TNT). Materials categorized as photolytic products ("P.P") could not be identified. If the controlling parameter is particle size and not purity; then dissolving any purity HNS-I in nitric acid and then drowning it in ice provides a new and different method of obtaining superfine HNS. The superfine HNS that precipitates out has about five times more surface area than the standard HNS from the Shipp synthesis. A typical example of this material is ID 2247. It was precipitated by the above method and chemical analysis (HPLC) shows 5.2% impurity (HNBiB). A surface area measurement shows 128,336 cm²/cm³ for this sample of explosive. This work is covered by Navy Patent Disclosure #5752 (Joseph C. Dacons).

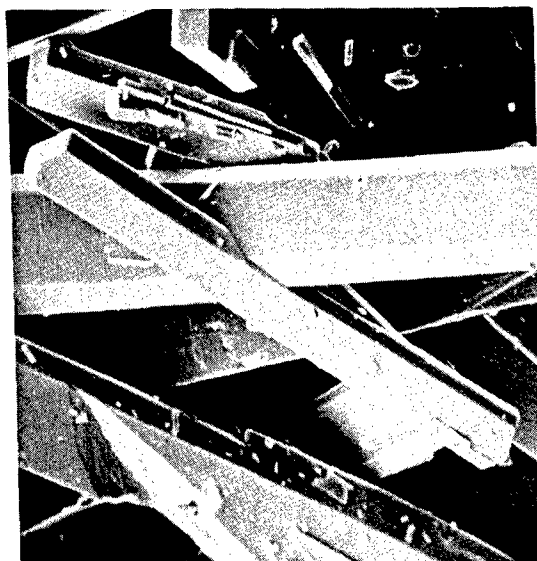
NITRIC ACID ASSAY FOR HEXANITROSTILBENE

Since detonating cords employing HNS use purified HNS (HNS-II), the conversion of HNS-I to HNS-II is of particular interest. To date, fuming nitric acid is the only solvent that has been found



250 X
7-26-77

ID 2302



250 X
7-26-77

ID 2304

1 cm = 40 μ



FIGURE 1. PHOTOMICROGRAPHS OF HNS (ID2302 AND 2304).

TABLE 1
VACUUM STABILITY TESTS AT 260°C

Compound	NSWC Ident.	Drying			Recrys. Solvent	cc/g 20 Min Surge	cc/g/hr 2 Hr Period
		Time, Hrs	Temp. °C	Pressure			
HNS-II	ID2155	16	120	Vacuum	Acetonitrile/ Toluene	0.37	0.19
HNS-II	2156	16	120	Vacuum	Acetonitrile/ Toluene	0.36	0.21
HNS-II	2157	4	120	Vacuum	90% HNO ₃	0.87	0.15
HNS-II	2158	16	120	Vacuum	Acetonitrile/ Xylene	0.46	0.24
HNS-II	2302	16	60	Atmos	90% HNO ₃	1.14	0.18
HNS-II	2304	16	120	Vacuum	90% HNO ₃	0.07	0.08
HNS-I	2276	16	120	Vacuum	90% HNO ₃ /H ₂ O	0.36	0.25
HNS-I	Project 96-8433-50D	16	120	Vacuum	90% HNO ₃ /H ₂ O	0.03	0.26
HNS-I	714	16	120	Vacuum	Acetonitrile/ Toluene	2.02	0.58
HNS-I	714	120	120	Vacuum	90% HNO ₃ /H ₂ O	1.63	0.80

TABLE 2
QUANTITATIVE HNS DATA - NAVAL SURFACE WEAPONS CENTER

Explosive Ident	<u>% HNS</u>	<u>% HNBiB</u>	<u>% TNB</u>	<u>% PiCH₂OH</u>	<u>% PiCHO</u>	<u>% TNT</u>	<u>% "P.P."</u>
2302*	99.6	0.2	None	None	0.3	None	None
2304**	99.8	0.3	--	--	--	--	--

*Nitric Acid Prep - Acid Assay 0.131%

**Nitric Acid Prep - Acid Assay 0.0111%

which produces high bulk density HNS-II by simple recrystallization procedures. This report describes a simple, convenient procedure for determining the concentration of nitric acid remaining in recrystallized HNS-II using a pH meter and a solvent mixture consisting of 90% H₂O and 10% DMSO by volume. The method was developed by Eleonore Kayser of this Center.

Experimental Results and Discussion

The solvent used in the assay was J. T. Baker Analyzed Reagent DMSO. The concentration of HNS-II ranged from 50 to 120 mgs per 10 ml of DMSO solvent. These initial stock solutions were heated to insure complete dissolution of the HNS-II. The 0.5 ml of the HNS-II stock solution was added to 4.5 mls of distilled water and thoroughly mixed. All data were determined on a Beckman Research pH meter with a combination pH/reference electrode.

ACS grade nitric acid was used to define a standard curve of acid concentration vs "pH meter reading" in a 90% H₂O/10% DMSO solvent mixture (Figure 2). For the greatest accuracy, the standard curve is determined concurrently with the HNS-II samples to be analyzed since DMSO is a highly hygroscopic solvent. The concentration of nitric acid in several HNS-II samples was obtained from the standard acid curve mentioned above. The weight percent of acid was then calculated from this data. The results for the HNS-II samples studied are summarized in Table 3 and show the weight percent of nitric acid found for several samples of HNS-II that have been dried under various conditions. Those samples dried under relatively stringent conditions (vacuum dried for 24 hours) show no evidence of residual nitric acid.

To determine the accuracy and reproducibility of the acid values obtained from the 90/10 mixture, two other H₂O/DMSO solutions, 50/50 and 10/90, were also studied. The resulting data (Table 3) show consistent acid values from the three H₂O/DMSO mixtures used and also for widely varying concentrations of HNS-II (0.5 to 4.5 mls). The hexanitrostilbene tested was prepared at the Naval Surface Weapons Center by nitric acid recrystallization.

Solutions of p-dioxane and water were also studied; however, acidity values could not be determined due to the relative insolubility of HNS in p-dioxane (max. so. 5 mg/10 ml).

THERMAL CONDITIONING OF DETONATING CORDS

The F-14 aircraft utilized detonating cords in the crew egress system. A thermal cycling performance specification that was applied to these cords is defined as follows:

The cords shall be stabilized at -65°F and maintained for a period of one hour. The temperature shall then be raised to

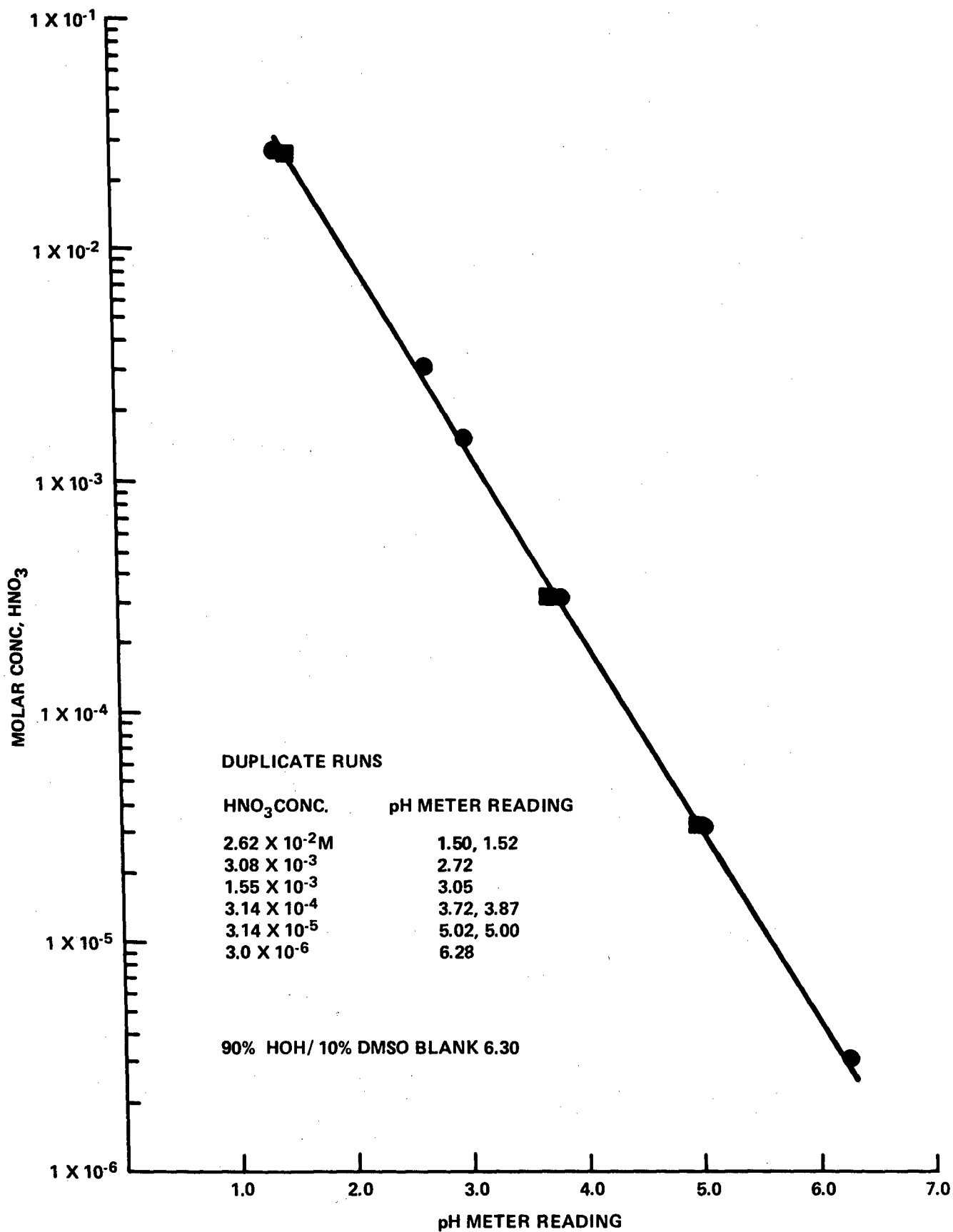


FIGURE 2. NITRIC ACID STANDARD CURVE IN 90% HOH/10% DMSO.

TABLE 3

HNS ACIDITY DATA

Explosive NSWC Ident ID	Weight % of Nitric Acid ^a HOH/DMSO Solvent System			Comments
	90/10	50/50	10/90	
2302	.01	--	--	b
2302	.01	--	--	b
2304	.13	--	--	c
2304	.13	--	--	c
2276	.02	.02	.02	d
2276	.02	.02	.02	d
2276	.00	.00	.00	e
2157	.06	.07	.06	c
2157	.07	.07	.06	c
2157	.00	.00	.00	e
2157	.00	.00	.00	e

- a. calculated from the HNS-II sample reading minus solvent blank
 b. vacuum dried at 130°C overnight
 c. dried in a warm oven at 60°C overnight
 d. dried in a warm oven at 60°C for 24 hours
 e. vacuum dried for 24 hours

+350°F and maintained for a period of 55 minutes. The temperature shall then be decreased to -65°F and stabilized for the start of the next cycle. The maximum transition time between temperatures shall be five minutes. The change in temperatures from -65°F to 350°F shall constitute one cycle of two hour duration. The cords shall be subjected to a minimum of 100 cycles. The performance of the cords are determined by detonation velocity measurements at room temperature.

The elevated temperature storage tests specified at NAVSWC, are considered to be penalization tests, and are not to be construed to be within the normal expectation of elevated temperatures for hardware performance. For these tests the following specification was implemented: The cords shall be placed in an oven preheated to 425°F until withdrawn from the oven at various predetermined intervals between two hours and 48 hours.

DETONATING CORD PERFORMANCE

The performance of the detonating cords was determined by measuring the detonation velocity from a short length of cord after exposure to the elevated temperature. In order to determine how each vendors cord would perform, the vendor was asked to fabricate cords from a given quantity of GFE (HNS). The cords were fabricated by each company according to their own proprietary method. The cords/vendors are identified as follows:

Ensign Bickford (EB)
Explosive Technology (ET)
Teledyne McCormick Selph (TMC)

DISCUSSION

Detonating cords fabricated by the above vendors were submitted to the thermal cycling specification parameters representative of those used on the Grumman F-14 Design Control Specification. The cords were cut into six (6) inch lengths and placed into copper refrigeration tubing with the ends of the tubes cold welded.⁶ This copper tube has proven to be a good test vehicle since it retains any degradation products (in the form of gases) typical of an SMDC design and protects the cords from abrasion. Following each test, the detonating cord was removed and the copper tube discarded. The detonating cord samples were placed on an aluminum plate, as shown in Figure 3. The electrical schematic for the probe circuit is shown in Figure 4. Detonation velocity results are shown in Table 4. The first interesting point to note is the loss of velocity in detonating cords (ID 1850), from magazine storage between 1974, and the latest testing in 1978. This was the first example of any evidence of degradation of an HNS cord in magazine storage. The acid recrystallized HNS in the cord performed well in the cycling

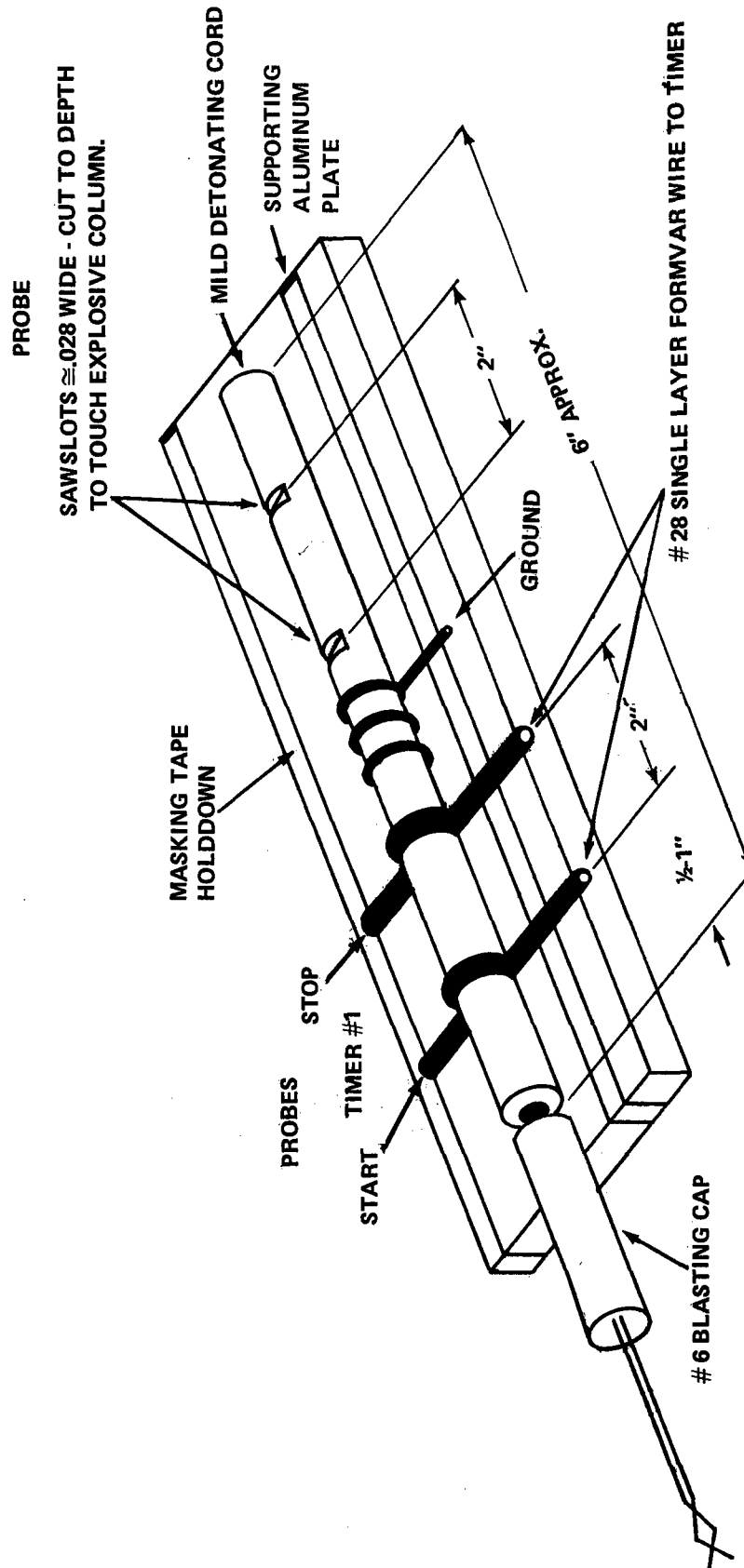


FIGURE 3. DETONATION VELOCITY MEASUREMENT FIXTURE

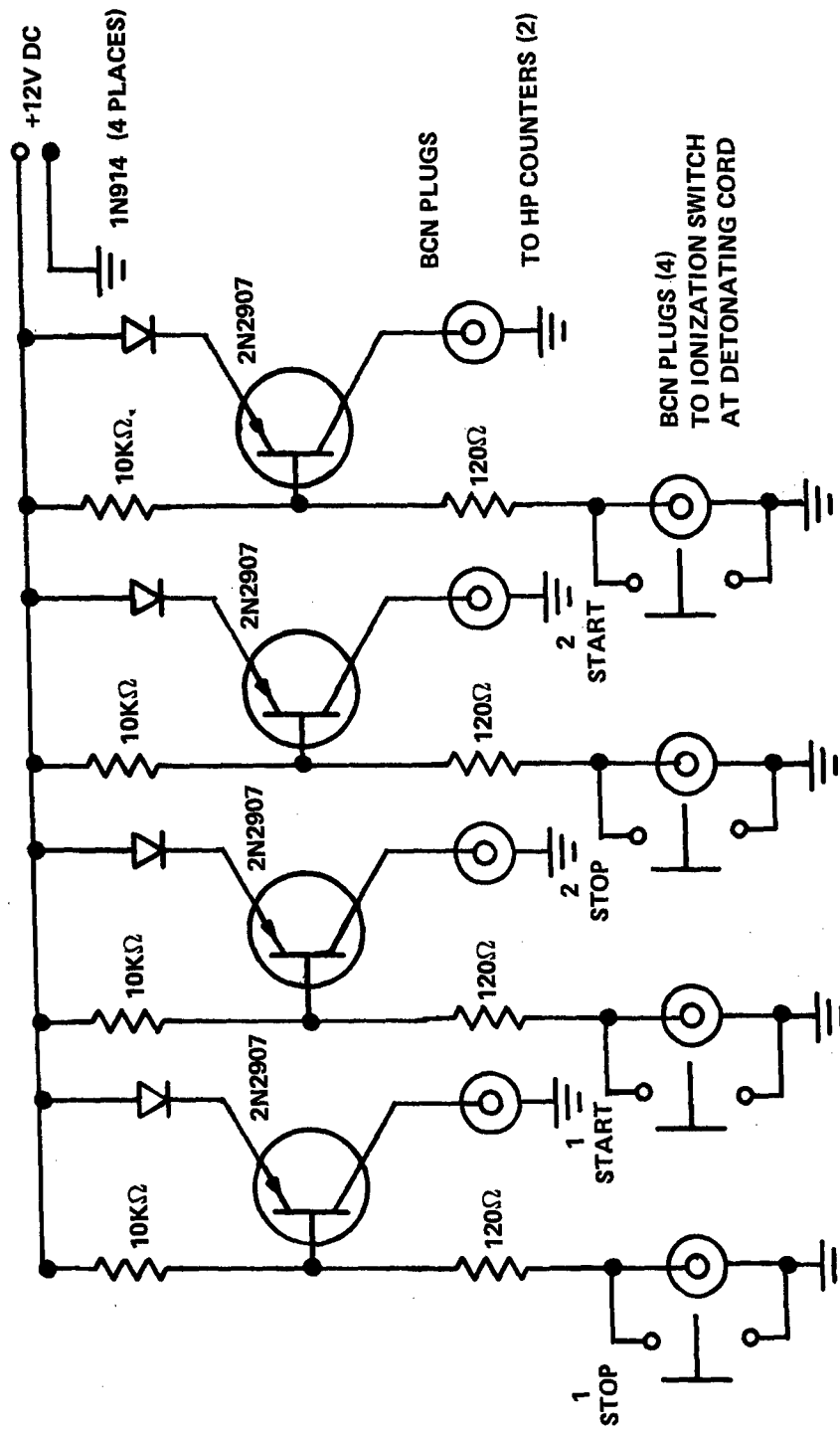


FIGURE 4. ELECTRICAL SCHEMATIC FOR MEASURING DETONATION VELOCITY OF DETONATING CORDS AT ELEVATED AND REDUCED TEMPERATURES.

TABLE 4
 DETONATING VELOCITY ELEVATED/LOW TEMPERATURE CYCLING OF HNS-II SILVER MDC
 (F-14 SPECIFICATION)

NAWSWC Expl. Ident. (Solvent)	Vendor	NAWSWC Cord	Year of Testing	Detonation Velocity (m/s)			
				Cycle 0	Cycles 48	Cycles 70	Cycles 100
ID 1859	ET	ID 1850	1974	7130	7175	7155	7031
ID 1859 (Acid)	ET	ID 1850	1978	6750	-	-	6414
ID 2304	EB	ID 2376	1978	6710	-	-	6271
ID 2302 (Acid)	EB	ID 2370	1978	6735	-	-	6196
ID 2304	ET	ID 2364	1978	6680	-	-	6441
ID 2302 (Acid)	ET	ID 2363	1978	6685	-	-	6460
ID 2302	T/M/C	ID 2345	1978	6860	-	-	6577
ID 2304 (Acid)	T/M/C	ID 2346	1978	7089	-	-	6791
Vendor Furnished WS5003E (Organic)	ET	ID 1977	1978	6191	-	-	6115

test shortly after fabrication in 1974 but now the results show degradation when submitted to the same test in 1978. The recently fabricated cords ID 2376, 2370, 2364, 2363, 2345 and 2346 also show degradation after the 100 cycle testing. These were fabricated by three different vendors using three different processes. The control samples fabricated from organic solvent recrystallized HNS (Procurement Specification WS5003E) did not show any degradation following the temperature cycling. The results of these tests indicate that the nitric acid recrystallized HNS explosive does not retain the desired thermal stability in detonating cords irrespective of the vendor fabrication process, or the residual acid in the HNS explosive.

Specifically, the cord sample ID 1850 not only had some degradation in normal magazine storage, prior to testing, but also began to degrade shortly after exposure at 425°F. Thermal decomposition was observed as a reduction of detonation velocity after four hours (t_4) and, finally, "inline" detonation failure around eight hours (t_8), Table 5. At twenty hours (t_{20}) the cord was so badly decomposed it could not be initiated by a standard #6 blasting cap. See Figure 5.

Coincidental with decomposition at (t_4), exudation of the explosive column was observed as a liquid medium and a dark column being forced out the ends of the 6" length cord. In order to better understand the physical/chemical change taking place in the explosive column, both neutron radiography and x-ray techniques were implemented.

Neutron radiography was conducted at the National Bureau of Standards, Reactor Radiation Division, Gaithersburg MD. On a per case basis, the detonating cords were placed forward of a pin hole collimator in the nuclear reactor with a 10^9 N/cm² @ 10KW flux on the samples for three hours. The samples were placed on photographic film at a distance from the reactor determined by an L/D of 180 where D=12" for the neutron beam. After several attempts to obtain the necessary film contrast and observe any voids that might be in the column of explosive, the method was abandoned.

The cords were then returned to NAVSWC, Metallic Materials Branch, where x-Ray was used as a method of determining whether voids existed in the explosive columns. A new technique of placing the film, screens, and MDC on a vacuum cassette to obtain better contact with the film was used. The following guidelines were used to x-ray the cords:

Energy - 175 KV
 Exposure - 10 mA, 7 min
 F.F.D. - 5'
 Screens - 0.005"F and 0.010"B (Pb or Ta)
 Film - Kodak R Film

TABLE 5

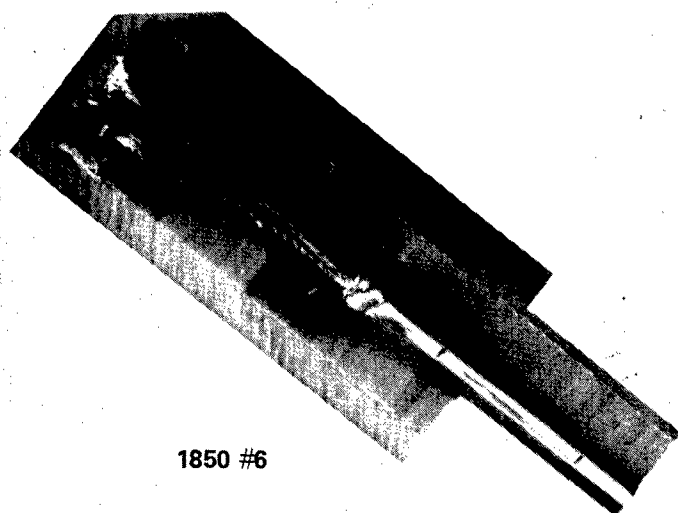
DETONATION VELOCITY/CHEMICAL ANALYSIS AFTER ELEVATED TEMPERATURE STORAGE
@ 425°F (HNS-II SILVER MDC*) (NAVSWC SPECIFICATION)

Testing Year	Exposure Time (Hours)	t ₀	t ₂	t ₄	t ₈	t ₂₀	t ₂₈	t ₃₂	t ₄₈	t ₅₆
1974	Detonation Velocity (m/s)	7130	-	6631	6250	-	-	5641	-	*Initi- ation Failure
1978	Detonation Velocity (m/s)	6750	6195	6161	**In Line Failure (detonation)	**Initiation Failure	**Initiation Failure			
1978	Remaining % HNS	100.0	-	100.0	81.3	17.6	3.4	-	-	-
	% Sol. Mat.	0.0	-	0.0	11.1	59.0	27.8	-	-	-
	% Insol. Mat.	0.01	-	0.01	5.8	23.4	68.8	-	-	-
	HNO ₃ Assay %	0.05	-	-	-	Expl column extruding from MDC sheath				

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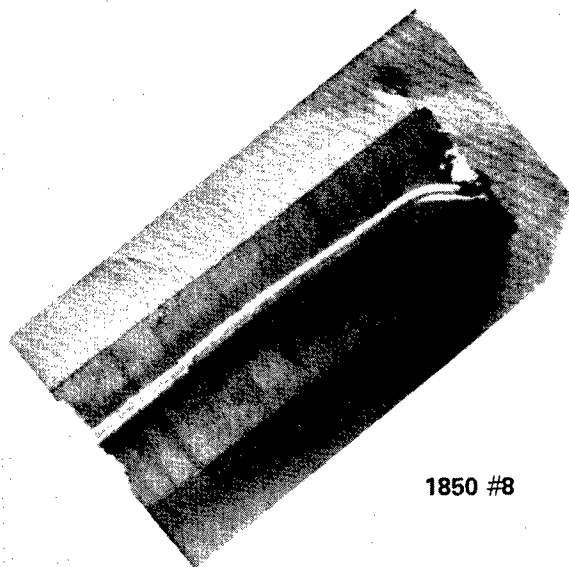
*ID 1850:HNS-II 2½ gr/ft. Silver Sheath - Vendor Explosive Tech (No annealing of cords)
Contains HNS-II ID 1859 (T/McC/S Lot 8203-2 Nitric Acid Recrys. HNS)

**Color Change in Solv. DMSO



t_8

SCALE: 1:1



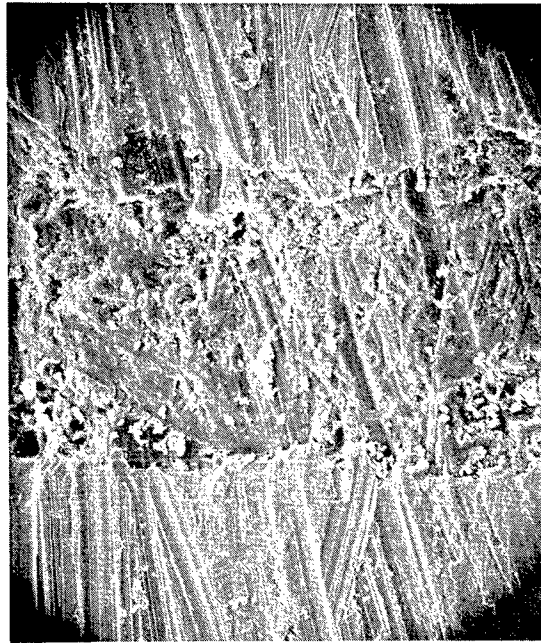
1850 #8

t_{20}

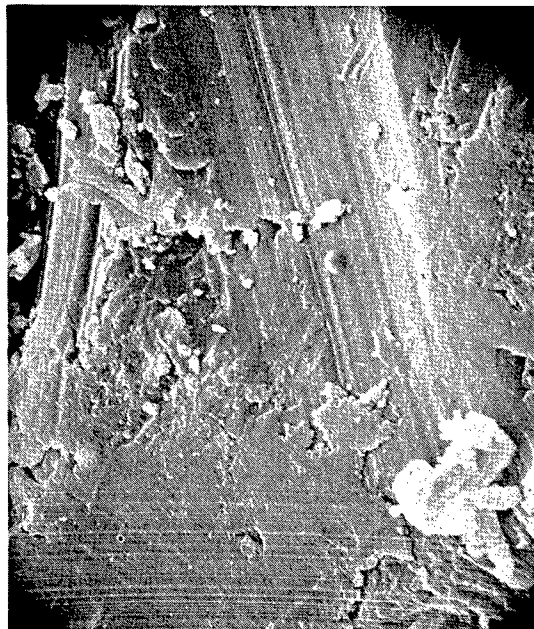
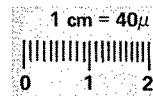
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FIGURE 5. DETONATING CORD PERFORMANCE AT TIMES t_8 AND t_{20} (ID1850).



250 X



2500 X

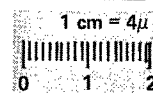


FIGURE 6. PHOTOMICROGRAPHS : ID1850 (CONTROL).



250 X

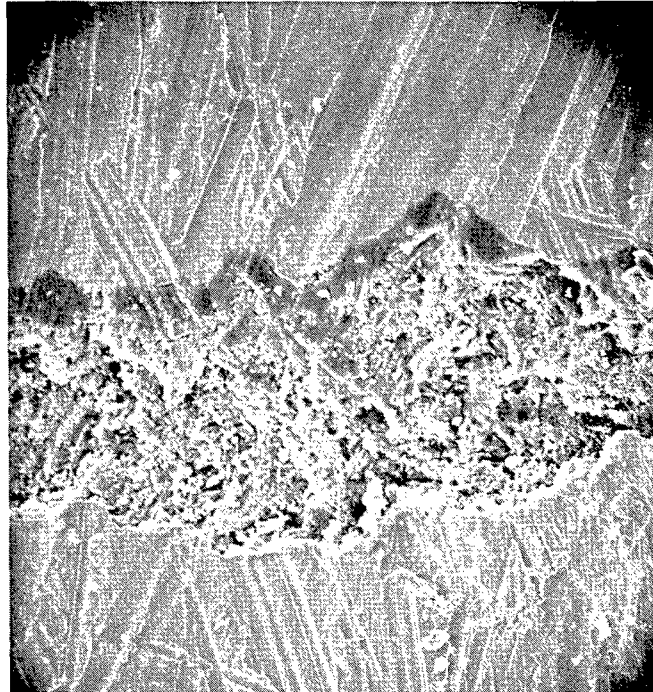
1 cm = 40 μ
0 1 2



2500 X

1 cm = 40 μ
0 1 2

FIGURE 7. PHOTOMICROGRAPHS: ID1850 AFTER 4 HRS. @425° F.



250 X

1 cm = 40 μ



2500 X

1 cm = 4 μ

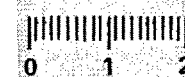


FIGURE 8. PHOTOMICROGRAPHS: ID1850 AFTER 20 HRS. @425° F.

The explosive column was less than 1/16" in diameter and was very difficult to analyze visually. However, voids were detected as variable density within the explosive column. This was later confirmed by a scanning electron microscope (SEM), as can be seen by comparing the explosive surfaces at 2500X of ID 1850 which has been cut to expose the explosive column of HNS of Figures 6, 7 and 8.

Changes in the crystal geometry of the explosive could not be seen in the X-Ray prints, but they were confirmed by the photomicrographs. The progressive physical/chemical change was more apparent after chemical analyses were made on the cord. High-performance liquid chromatography (HPLC) was used to analyze the explosive/degradation products at several sampling times during the exposure. Consistent with the loss of detonation velocity, the DMSO solvent showed a darkening, which indicated the presence of soluble impurities not observed in the original sample. An assay showing the percentage of HNS remaining after various exposure times revealed nearly 20% of the HNS had decomposed into other materials after eight hours; more than 80% decomposed after 28 hours. The chemical assays are shown in detail in Table 5. The decrease in the detonation velocity between t_0 and t_2 is probably an "annealing" effect or relaxation in the explosive column brought about by the elevated temperature exposure. At t_4 , the chemical assay shows 100% HNS remaining, therefore, the decomposition does not begin to take place until after four hours exposure to 425°F. HNS cords ID 2364 and ID 2345 were exposed and analyzed to show the same characteristics of exudation, voids, and degradation of detonation velocity. Chemical analyses were not made except at t_0 and t_{48} . The results in Table 6 show a degradation occurring both chemically and in the detonation velocities. There is a hint of improvement of explosive performance in ID 2364 over that of ID 2345 since the residual acid is less and the percent HNS is higher in ID 2364.

The organic solvent recrystallized material (ID 1977) was exposed at the same time as the acid material in question. There wasn't any significant change in the detonation velocity after exposure for two days @ 425°F. The values are shown in Table 7 and may be compared with results from the same test run in 1975.

CONCLUSIONS

1. Hexanitrostilbene can be recrystallized from nitric acid and with proper drying procedure can be processed relatively free of acid.
2. It has been determined that a small amount of residual nitric acid, as low as 0.05%, has caused a significant loss of performance in detonating cords from normal magazine storage over a period of four years time.

TABLE 6

DETONATION VELOCITY/CHEMICAL ANALYSIS AFTER ELEVATED TEMPERATURE STORAGE
@ 425°F (HNS-II SILVER MDC) (NAVSWC SPECIFICATION)

NAVSWC ID 2364*	t ₀	t ₂	t ₄	t ₈	t ₂₀	t ₂₈	t ₃₂	t ₄₈	t ₅₆
Detonation Velocity (m/s)	6680	6441	6343	6277	6323	6222	-	Failure	-
				Color Change in Solution (DMSO)					
Remaining % HNS	100.0	-	-	-	-	-	-	14.8	-
A									
% Solvent	0	-	-	-	-	-	-	7.4	-
S									
% Insol.	0	-	-	-	-	-	-	77.8	-
A									
Y									
Acid Assay %	0.01							Expl column extruding from MDC sheath	
ID 2345*									
Detonation Velocity (m/s)	6860	6672	6464	Failure	Failure	Failure	-	Failure	-
				Color Change in Solv. (DMSO)					
Remaining % HNS	100.0	-	-	-	-	-	-	7.8	-
A									
% Sol. Mat.	0	-	-	-	-	-	-	16.7	-
S									
% Insol.	0	-	-	-	-	-	-	75.4	-
A									
Y									
Acid Assay %	0.13							Expl Column extruding from MDC sheath	

*ID 2364 HNS-II 2½ gr/ft. Silver Sheath - Vendor: Explosive Tech (No annealing of Cords)
Contains HNS-II ID 2304 (NSWC 96-8433-61B, Nitric Acid Recrys. dried @135°C under vacuum for 16 hrs)

**ID 2345 HNS-II 2½ gr/ft. Silver Sheath - Vendor: Tel/McC/Selph (Fab. anneal @450°F 1 hour)
Contains HNS-II ID 2302 (NSWC 96-8433-61A, Nitric Acid Recrys. Air Dried @55°C for 16 hours)
Additional Drying by vendor @52°C for 16 days

TABLE 7

DETONATION VELOCITY AFTER ELEVATED TEMPERATURE STORAGE
@ 425°F (HNS-II SILVER MDC)* (NAVSWC SPECIFICATION)

Year of Test	Exposure Time (hrs)	t ₀	t ₂	t ₄	t ₈	t ₂₀	t ₂₈	t ₃₂	t ₄₈	t ₅₆	t ₇₃	t ₁₀₀	t ₂₆₄
1975	Detonation Velocity (m/s)	6056	-	6045	6014	-	-	6050	-	5979	6072	5986	5996
1978	Detonation Velocity (m/s)	6191	6083	6088	6049	6013	6071	-	5961	-	-	-	-

*ID1977: HNS-II 2½ gr/ft Silver Sheath-Vendor: Explosive Tech (No Annealing of Cords)
Contains HNS-II (Tel/McC/S Lot 3565-1, WS 5003E, Organic Solvent Recrys)

3. The performance of cords with 0.01% and 0.13% residual nitric acid had been reduced when submitted to the 100 cycle temperature environment in the F14 design control specification.
4. Further penalization of the detonating cords by elevated temperature storage at 425⁰F supports the findings from the temperature cycling tests and point out the fact that the HNS explosive processed by using organic solvents will survive the thermal environment better than the acid material in the same cord configuration.
5. The technique of using chemical analysis to determine the remaining explosive and contaminants, combined with detonation velocity measurements, is a viable method of assessing failures or potential failures in detonating cords.

REFERENCES

1. Shipp, K. G., "Heat Resistant Explosives XIV. Synthesis and Properties of 2,2', 4,4', 6,6' - Hexanitrostilbene, HNST," NOLTR 62-107, 15 Jun 1962.
2. Shipp, K. G., "Heat Resistant Explosives XVI A New Synthesis of 2,2', 4,4', 6,6' - Hexanitrostilbene, HNS," NOLTR 64-34, 22 Apr 1964.
3. Taylor, Francis Jr., et al "Heat Resistant Explosives, XX. Production of Grade II HNS," NOLTR 65-142, 26 Aug 1965.
4. Syrop, Leroy J., "Process for Recrystallizing Hexanitrostilbene," U. S. Patent 3,699,176, 17 Oct 1972.
5. Kayser, Eleonore G., "Analysis of 2,2', 4,4', 6,6' - Hexanitrostilbene (HNS) By High Performance Liquid Chromatography," NSWC/WOL TR 77-154, 14 Mar 1978.
6. Kilmer, E. E., "Detonating Cords Loaded with Hexanitrostilbene (HNS) Recrystallized from Acid or Organic Solvents," NSWC/WOL TR 75-142, 2 Sep 1975.

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